Report 2240

QUANTITATIVE DETERMINATION OF MONOETHANOLAMINE AND GLYCOL ETHERS IN CARBON-REMOVING COMPOUNDS

by

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The continuing investigation to develop analytical methods for control of Federal and Military Specification products has resulted in a single method for the determination of monoethanolamine and the glycol ethers in Federal Specification P-C-111D, Carbon-Removing Compound.

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PREFACE

Authority for the work covered by this report is contained in Project 1L162105AH84.

The period covered is 1977.

The investigation was performed by T. Nichols and reviewed by M. Adams under the supervision of E. J. York, Chief, Material Technology Laboratory, MERADCOM, Fort Belvoir, Virginia.

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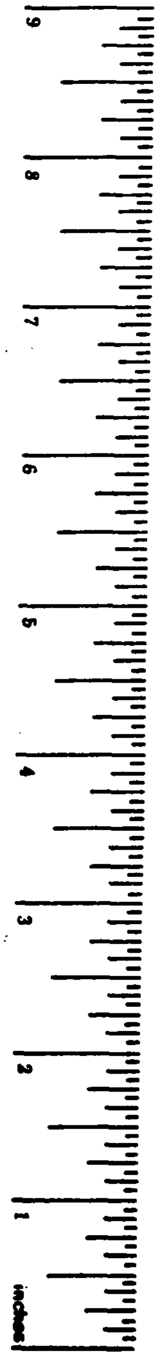
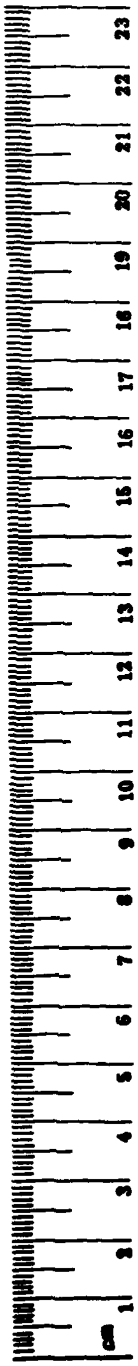
Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	metric tons	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	L
pt	pints	0.47	liters	L
qt	quarts	0.95	liters	L
gal	gallons	3.8	liters	L
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

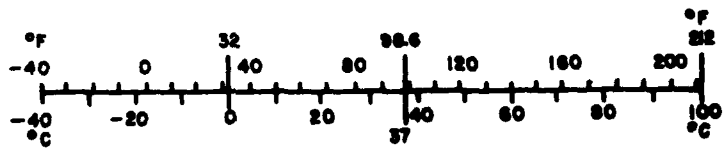
* 1 in = 2.54 cm (exactly).





Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10 000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	metric tons (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
L	liters	2.1	pints	pt
L	liters	1.06	quarts	qt
L	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



QUANTITATIVE DETERMINATION OF MONOETHANOLAMINE AND GLYCOL ETHERS IN CARBON-REMOVING COMPOUND

I. INTRODUCTION

1. **Subject.** The object of this investigation was to develop an improved method for the determination of monoethanolamine in carbon-removing compounds.

2. **Background.** Carbon removers and other types of metal conditioners frequently incorporate glycol ethers and ethanolamines in their formulations. These materials have proved effective in performance and satisfactory in cost. The formulated products are generally procured by the Government on a low-bid basis for a specification product. To guarantee the quality of the purchased product, satisfactory methods for chemical analysis must be developed and included in the specification.

Monoethanolamine and three glycol ethers are required ingredients in the carbon-removing compound of Federal Specification P-C-111D as shown in Table 1.

Table 1. Composition Requirements for Federal Specification P-C-111D, Carbon-Removing Compound

Ingredient	Requirements, Percent by Volume
Monoethanolamine	21.0 min.
Ethylene glycol monobutyl ether	9.0 min.
Diethylene glycol monomethyl ether	5.0 min.
Diethylene glycol monobutyl ether	3.0 min.
Water	55±3

The material which meets all of the specification requirements approximates the comparison formula of P-C-111D (Table 2).

The literature presents several methods for the quantitative analysis of monoethanolamine. These include a gas-liquid chromatographic determination as a trifluoroacetyl derivative,[1] a nonspecific acidic titration,[2] various colorimetric methods, and separation by column ch... ...ography.[3] The nonspecific acidic titration method is currently employed in Federal Specification P-C-111D but is obviously a

[1] L. E. Brydia and H. E. Persinger, Analytical Chemistry 39, No. 11, 1318-1320 (1967).

[2] Sidney Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley and Sons, Inc., 423 (1963).

[3] D. D. Christiansen *et al*, Analytical Chemistry 32, 874 (1960).

Table 2. Comparison Formula for P-C-111D, Carbon-Removing Compound

Ingredient	Percent by Volume
Ethylene glycol monobutyl ether	9.0
Diethylene glycol monobutyl ether	3.9
Diethylene glycol monomethyl ether	6.0
Monoethanolamine	21.5
Nonionic Surfactant	2.0
Oleic acid	2.0
Sodium silicate solution (0.25% by volume of 40° Baumé solution in distilled water)	55.6

poor method because of the possible presence of interfering alkaline materials. Because of interferences, the other methods were found to be unsuitable without time-consuming preliminary separations.

The procedure developed in this investigation is completely satisfactory for the simultaneous quantitative determination for both the monoethanolamine and the glycol ethers in the P-C-111D carbon remover. The method is intended to replace the nonspecific titration method now used for monoethanolamine and the more cumbersome column- and gas-chromatographic (GC) method used for the glycol ethers.

II. DETAILS OF TEST

3. **Instrumental Analysis.** The method employs gas-liquid chromatography utilizing a thermal conductivity detector and a two-column system:

a. Precolumn: 4-inch-long by 1/8-inch-outside diameter, teflon-coated stainless steel packed with 20-percent SE-30 on 60-80-mesh chromosorb WAW.

b. 6-foot-long by 1/8-inch-outside-diameter, teflon-coated stainless steel packed with 10-percent Reoplex 400 on 80-100-mesh chromosorb WHP.

The GC operating parameters are as follows: glass-lined injection port, 250° C; carrier (helium) flow, 25 ml/minute; thermal conductivity detector, 300° C; initial column oven temperature, 125° C; rate of oven temperature increase, 1° C/minute; final oven temperature, 165° C; length of run, 40 minutes.

4. **Calculations.** Chromatogram peaks are identified in the usual way by relative retention times. Correction factors are determined from compositions of known concentrations. Concentrations in percent by volume are calculated from the commonly used equation:

$$C = \frac{ADF}{B}$$

where A is the area under the peak in question, B is the area under the internal standard peak, D is the concentration of the internal standard, and F is the correction factor.

5. **Preparation of Sample.** Pipette 20 ml of the material to be analyzed and 2 ml of the internal standard, hexyl carbitol, into a 100-ml beaker. Mix with a glass stirring rod. Add 10 g of anhydrous K_2CO_3 and stir until it is dissolved. This material will at first become pasty but with a few minutes of further stirring will go into solution. Transfer the solution to a 125-ml separatory funnel and let separate. Discard the lower layer and transfer the top layer to a 50-ml glass-stoppered Erlenmeyer flask. Add 10 ml n-butanol to the flask, stopper, and mix gently. Add 20 g of anhydrous K_2CO_3 and shake the flask vigorously for 2 minutes. Let the solution settle, then decant it into a centrifuge tube. Stopper and centrifuge until the solution is clear. Using a 5-μl syringe, inject a 2-μl sample into the injection port of the gas-liquid chromatograph operated under the conditions specified in paragraph 3.

6. **Results.** The final sample prepared by this method for gas chromatographic analysis contains the glycol ethers, monoethanolamine, water (about 5 percent of the product), and the nonionic surfactant. The nonionic surfactant and other high-boiling-point materials that may be present in commercial samples are not determined but, instead, are trapped on the precolumn which is replaced periodically to maintain satisfactory and reproducible peak resolution.

Figure 1 is a typical chromatogram of a known material formulated to meet all of the requirements of P-C-111D. This single chromatogram suffices for the quantitative determination of monoethanolamine and the three required glycol ethers. Table 3 compares the results obtained with the true concentrations.

Figure 2 illustrates a commercial sample which meets the requirements of P-C-111D. Table 4 compares the analytical results from the chromatogram with the composition claimed by the manufacturer. Again the close agreement confirms the reliability of the method.

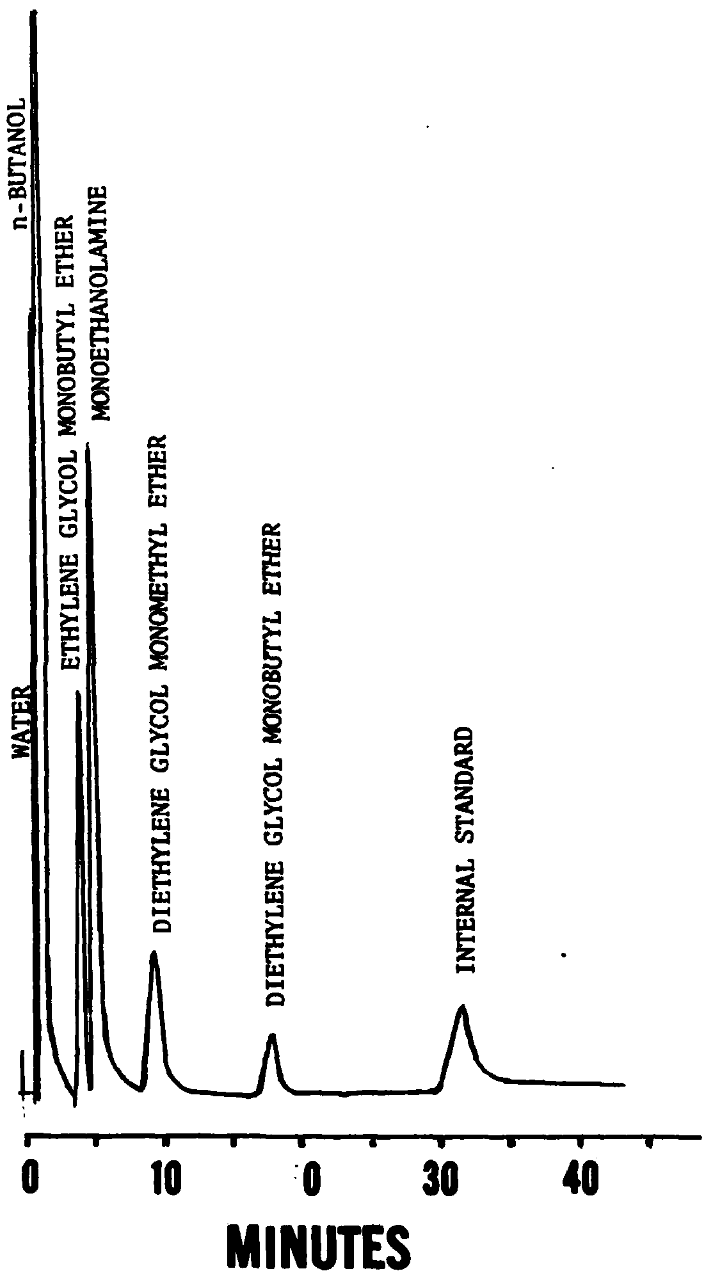


Figure 1. Chromatogram of a carbon-removing compound formulated to meet all of the requirements of P-C-111D.

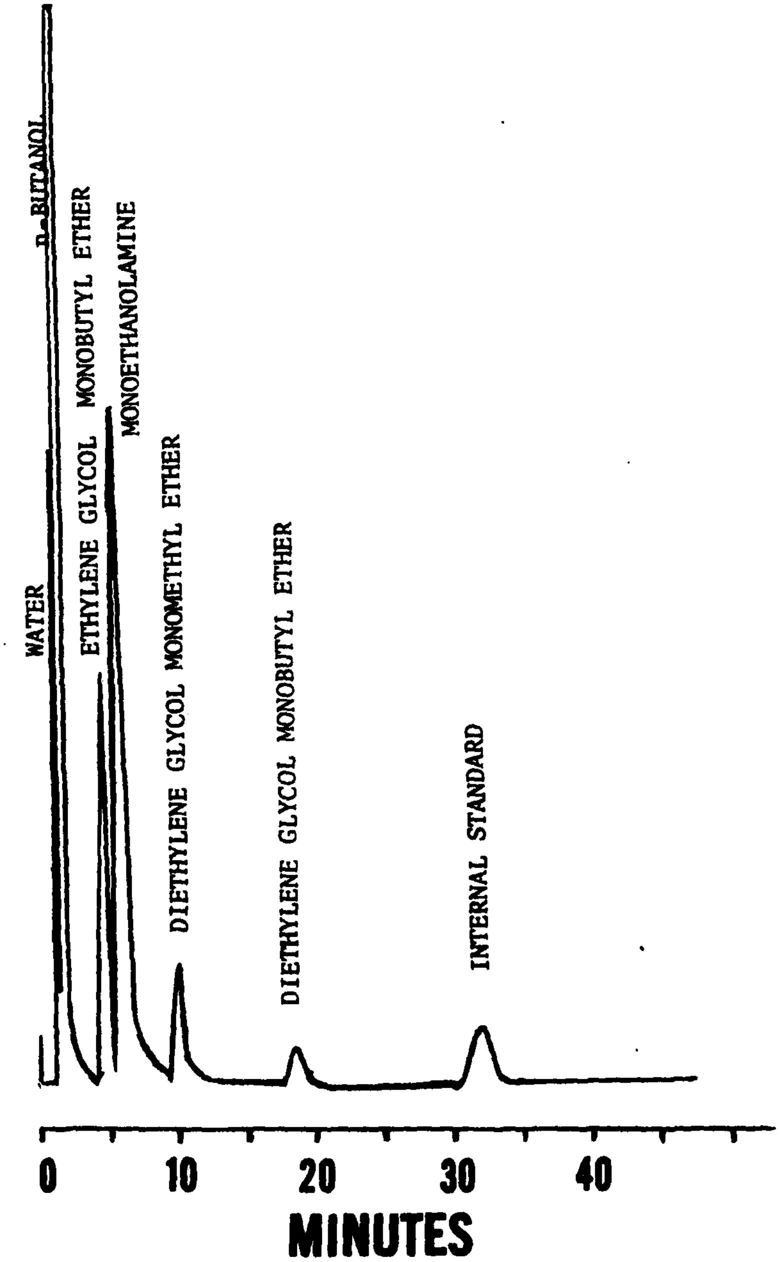


Figure 2. Chromatogram of a commercial carbon-removing compound.

Table 3. Analysis of Carbon-Removing Compound with Known Concentrations

Ingredient	Concentration, Volume Percent	
	Known	Found
Ethylene glycol monobutyl ether	10.0	9.9
Monoethanolamine	18.0	18.4
Diethylene glycol monomethyl ether	5.0	5.1
Diethylene glycol monobutyl ether	5.0	5.0
Detergent, nonionic	2.0	Not determined
Oleic acid	2.0	Not determined
Sodium silicate solution (0.25 percent by volume of 40° Baume' solution in distilled water)	58.0	Not determined

Table 4. Analytical Results Compared to Claimed Composition of a Commercial Sample of Carbon-Removing Compound

Ingredient	Volume Percent	
	Found	Claimed
Ethylene glycol monobutyl ether	9.1	9.4
Monoethanolamine	21.8	21.7
Diethylene glycol monomethyl ether	5.2	5.3
Diethylene glycol monobutyl ether	3.2	3.6

III. CONCLUSION

7. *Conclusion.* A gas chromatographic method was developed for the simultaneous quantitative determination of monoethanolamine and the glycol ethers in carbon-removing compounds similar to that covered by Federal Specification P-C-111D. The method can replace the two methods used for the quantitative determination of these materials. The method has important advantages. It is less time-consuming than the current method for the glycol ethers. The identification of the monoethanolamine by its peak retention time is regarded as a positive qualitative test, which is lacking in the nonspecific method now used.

The method developed will be recommended for inclusion in Federal Specification P-C-111D.